

Europium Coordination Compound with Highly Improved Luminescent Quantum Yield[⊕]

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ABSTRACT The luminescent properties of two Eu³⁺ compounds based on quinoline-2-carboxylic acid (Hqc), [Na₂Eu₂(qc)₆(CH₃COO)₂(H₂O)₄]·2DMF (**1**) and [Eu₂(qc)₆(H₂O)₆]·3H₂O (**2**), as well as their syntheses and structures are reported. Both compounds are formed by slow evaporation at room temperature and exhibit zero dimensional dinuclear structures. It is worth mentioning that a 4.5-fold enhancement in luminescent quantum yield is achieved by reducing the nonradiative deactivation, through which the quantum yield increases remarkably to 67.62% for **1** compared with 12.18% for **2**.

Keywords: Eu³⁺ compound; coordination environment; luminescent quantum yield;

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1 INTRODUCTION

The fascinating luminescence of lanthanide that covers the visible and infrared light is continually drawing attention to their applications in biomedical analysis and imaging, luminescent probes and sensors, as well as the security related materials, for instance security inks and barcodes^[1-7]. Luminescent quantum yield is essentially the very important parameter related to its applications mentioned above. Actually, the forbidden

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and faint $4f$ -to- $4f$ electronic transitions of lanthanide make their absorption coefficient small. As a consequence, direct excitation of the lanthanide ions rarely yields high luminescent materials. Lanthanide compounds, with organic ligand function as light antenna overcoming the weak absorption, have been increasingly studied, especially those based on π -conjugated ligands^[8-18]. And their quantum yields are basically depending on the following processes: light absorption and energy transfer between ligand and lanthanide, followed by lanthanide emission^[19, 20]. In order to get luminescent materials with high quantum yield, some major problems should be solved: firstly, choosing the ligand with suitable triplet state to match well with the emitting level of the lanthanide ions^[21-23], and secondly, avoiding or reducing the influence of deactivation process mainly caused by OH vibration, because the lanthanide ions, especially Eu^{3+} ion, are extremely sensitive to it^[24, 25]. To date, the largest quantum yield of Eu^{3+} compound is reported up to 85%^[26]. Some further efforts are also devoted to improving the luminescence of lanthanide compounds, and further efforts will be continually made to gain luminescent materials with high quantum yield.

In consideration of the above discussions, combined with our previous work that the triplet state of quinoline containing ligand matches well with the $^5\text{D}_4$ emission state of Eu^{3+} ion^[27], herein, we report the syntheses, X-ray single-crystal structures and luminescence properties of two Eu^{3+} compounds based on quinoline-2-carboxylic acid (Hqc).

2 EXPERIMENTAL

2.1 Materials and instruments

All reagents and solvents were purchased commercially and used without further purification. The single-crystal structure data were determined by a Rigaku Saturn 724+ CCD diffractometer equipped with graphite-monochromatic $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation using the ω -scan mode at 123 K. Thermogravimetric analysis was carried out in the temperature range of 30~900 °C at a heating rate of 15 °C/min on a NETZSCH STA 449C instrument. Powder X-ray diffraction (PXRD) pattern was collected on a RIGAKU-DMAX 2500 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Steady-state photoluminescence spectra were recorded on a Horiba Jobin Yvon Fluorolog-3 spectrophotometer analyzer, and the time-resolved luminescence was performed on an Edinburgh Instruments FLS920 spectrofluorometer equipped with both continuous (450 W) and pulse xenon lamps.

2.2 Syntheses of compounds 1 and 2

Eu(CH₃COO)₃·6H₂O (0.41 mmol, 180 mg), CH₃CH₂ONa (0.60 mmol, 41 mg) and Hqc (0.62 mmol, 108 mg) were added to 20 mL CH₃CH₂OH, and stirred for 24 h. Colorless prism-shaped compound **2**, formulated as [Eu₂(qc)₆(H₂O)₆·3H₂O], was formed by evaporating the filtrate. And the resulting pale-white precipitate was then dissolved in 10 mL DMF and 3 mL H₂O. After slow evaporation at room temperature, colorless block crystals of compound **1**, formulated as [Na₂Eu₂(qc)₆(CH₃COO)₂(H₂O)₄·2DMF], were obtained.

2.3 Structure determination

The single-crystal structure data of compound **1** were determined by Saturn724+ CCD diffractometer with graphite-monochromatized MoK α (λ = 0.71071 Å) radiation at 123 K. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-97 program^[28, 29]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of hydrogen atoms on the organic ligands were generated geometrically and refined using a riding model while hydrogen atoms of water molecules were set according to Fourier difference maps. The selected bond lengths and bond angles of compound **1** are listed in Table 1.

3 RESULTS AND DISCUSSION

3.1 Crystal structure

Herein, the structure of compound **1** is illustrated specifically. According to single-crystal X-ray diffraction analysis, compound **1** crystallizes in the monoclinic $P2_1/c$ space group with a = 13.785(5), b = 18.776(6), c = 15.743(4) Å, β = 121.41(2)°, V = 3478(2) Å³, Z = 4, T = 123 K, D_c = 1.642 g cm⁻³, $F(000)$ = 1782, μ = 1.883 mm⁻¹, $GOOF$ = 1.049, R = 0.0193 and wR = 0.0476 ($I > 2\sigma(I)$). In the asymmetric unit, there are one europium ion, three qc⁻ ligands, one sodium ion and two water molecules that coordinate to the sodium ion, one coordinated acetic anion, and one lattice DMF molecule. As shown in Fig. 1, the Eu³⁺ ion exhibits a nine-coordinated geometry formed by five carboxylate oxygen atoms from four qc⁻ ligands, three carboxylate oxygen atoms from two acetic anions, and one pyridyl nitrogen atom. The Eu–O bond lengths vary between 2.341 and 2.555 Å, and the Eu–N bond is 2.715 Å (Table 2). The Eu³⁺ ion and its symmetry generated one are linked by four carboxylate groups from qc⁻ ligand and acetic acid to generate a dinuclear “Eu-dimer” that is enclosed by six qc⁻ ligands and two six-coordinated Na⁺ ions, as shown in Fig. 2a. The distance of Eu··Eu within “Eu-dimer” is 3.911 Å. A 3D supramolecular crystal building of compound **1** is constructed by π - π interaction and hydrogen bonds (Fig. 3, Table 2). It is worth noting that strong hydrogen bonds O–H··O and

O—H \cdots N contribute to the stabilization of the 3D structure (O—H \cdots O 2.772(2)~2.837(2) Å and 164~176 °). The quinoline rings of the nearby dinuclear “Eu-dimer” are almost parallel, thus π - π interaction between rings N(2)#2—C(11)#2—C(12)#2—C(13)#2—C(14)#2—C(15)#2—C(16)#2—C(19)#2—C(17)#2—C(18)#2 and N(3)—C(23)—C(24)—C(25)—C(26)—C(27)—C(28)—C(29)—C(30)—C(31) is formed (symmetry code: #2, $x+1$, $-y+1/2$, $z+1/2$). Within such π - π interaction, the inter-centroid distance and the dihedral angle are respectively 3.702 Å and 4.783 °, and the perpendicular distances of quinolone centroid on its counterpart involved are 3.371 and 3.471 Å. The crystallization DMF molecule is placed in the intermolecular region, establishing strong C—H \cdots O and O—H \cdots O hydrogen bonds. Analogously, compound **2**^[30] also displays a dinuclear “Eu-dimer” structure by the way of two Eu³⁺ ions surrounded by six q^- ligands, with six water molecules coordinating to the Eu³⁺ ions (Fig. 2b).

3.2 Power X-ray diffraction (PXRD) pattern and thermal stability analysis

The purity of compound **1** confirmed by powder X-ray diffraction is in agreement with the simulated one (Fig. 4), confirming the phase purity of the as-synthesized product. Compound **1** keeps stable until 285 °C according to the thermogravimetric analysis as shown in Fig. 5. Two coordinated water and lattice DMF molecules are lost during the temperature range of 20~185 °C (found, 12.72; calcd. 12.74%). Then compound **1** is stable up to 285 °C. Finally, the framework decomposes abruptly with further heating.

3.3 Luminescent property

The solid state emission spectra of compounds **1** and **2** excited at 350 nm are shown in Fig. 6. The characteristic $^5D_0 \rightarrow ^7F_J$ ($J = 0 \sim 4$) transitions of Eu³⁺ ion show main emission bands at 578, 591, 614, 649, and 698 nm respectively, with the hypersensitive $^5D_0 \rightarrow ^7F_2$ transition at 614 nm dominating the spectra. The splitting of the emission band due to the effect of ligand-field indicates that Eu³⁺ ions lie in the low symmetry. No broad emission band resulting from the ligand is observed, which means the ligand transfers the absorbed energy effectively to the emitting level of the Eu³⁺ ion. It is worth emphasizing that the quantum yield of compound **1** is up to 67.62%, which is 5.5 times as much as the quantum yield (12.18%) of compound **2**, in spite of the same ligand antenna. Clearly, the avoiding of nonradiative deactivation process associated with the OH vibration accounts for the high luminescence efficiency of compound **1**. Actually, no coordinated water exists in the inner coordination sphere of the Eu³⁺ ion in compound **1**, whereas there are six water molecules coordinating to Eu³⁺ ion in compound **2**. It is hypothesized that the coordination of acetic acid as well as sodium ion which water molecules coordinate to in compound **1** results in better shielding of the Eu³⁺ center, leading to the enhancement of quantum yield. In addition, the coordination of sodium ion can reduce

the vibration of framework causing the enhancement of luminescent quantum yield. Therefore, for the purpose of getting lanthanide compounds with high luminescence quantum yield, removing water from the coordination sphere is required.

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Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for Compound 1

Bond	Dist.	Bond	Dist.
Eu(1)–O(2)	2.3410(13)	Eu(1)–O(5)#1	2.5133(13)
Eu(1)–O(5)	2.3782(13)	Eu(1)–O(6)#1	2.5268(15)
Eu(1)–O(3)	2.3887(13)	Eu(1)–O(7)	2.5552(13)
Eu(1)–O(8)	2.4319(15)	Eu(1)–N(1)	2.7152(14)
Eu(1)–O(4)#1	2.4660(13)		
Angle	(°)	Angle	(°)
O(2)–Eu(1)–O(5)	142.21(4)	O(8)–Eu(1)–O(6)#1	145.74(5)
O(2)–Eu(1)–O(3)	141.91(4)	O(4)#1–Eu(1)–O(6)#1	107.16(4)
O(5)–Eu(1)–O(3)	73.41(5)	O(5)#1–Eu(1)–O(6)#1	51.42(4)
O(2)–Eu(1)–O(8)	72.57(5)	O(2)–Eu(1)–O(7)	112.86(4)
O(5)–Eu(1)–O(8)	92.83(5)	O(5)–Eu(1)–O(7)	80.87(4)
O(3)–Eu(1)–O(8)	131.14(4)	O(3)–Eu(1)–O(7)	79.14(4)
O(2)–Eu(1)–O(4)#1	71.07(4)	O(8)–Eu(1)–O(7)	52.17(4)
O(5)–Eu(1)–O(4)#1	71.22(4)	O(4)#1–Eu(1)–O(7)	114.32(5)
O(3)–Eu(1)–O(4)#1	139.04(4)	O(5)#1–Eu(1)–O(7)	150.81(4)
O(8)–Eu(1)–O(4)#1	70.90(4)	O(6)#1–Eu(1)–O(7)	138.06(4)
O(2)–Eu(1)–O(5)#1	96.15(4)	O(2)–Eu(1)–N(1)	64.28(4)
O(5)–Eu(1)–O(5)#1	73.84(5)	O(5)–Eu(1)–N(1)	149.37(4)

O(3)–Eu(1)–O(5)#1	79.84(4)	O(3)–Eu(1)–N(1)	88.07(4)
O(8)–Eu(1)–O(5)#1	141.97(4)	O(8)–Eu(1)–N(1)	81.04(5)
O(4)#1–Eu(1)–O(5)#1	71.09(5)	O(4)#1–Eu(1)–N(1)	132.56(4)
O(2)–Eu(1)–O(6)#1	74.60(5)	O(5)#1–Eu(1)–N(1)	127.53(4)
O(5)–Eu(1)–O(6)#1	119.52(4)	O(6)#1–Eu(1)–N(1)	76.14(4)
O(3)–Eu(1)–O(6)#1	73.58(5)	O(7)–Eu(1)–N(1)	71.65(4)

Symmetry code: #1: $-x+1, -y+1, -z+1$

Table 2. Selected Hydrogen Bond Lengths (Å) and Bond Angles (°) for Compound 1

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
O(9)–H(9A)···O(10)#1	0.85	1.93	2.772(2)	172
O(9)–H(9B)···O(1)	0.90	1.95	2.825(2)	164
O(10)–H(10B)···O(11)	0.97	1.87	2.837(2)	173
O(10)–H(10A)···N(3)#2	0.91	1.92	2.828(2)	176

Symmetry codes: #1: $2-x, 1-y, 2-z$; #2: $2-x, 1/2+y, 3/2-z$

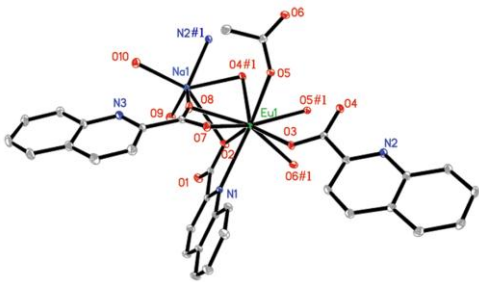


Fig. 1. Coordination environment (30% ellipsoids) of Eu^{3+} ion in compound 1, in which hydrogen atoms and solvent are omitted for clarity (#1: $-x+1, -y+1, -z+1$)

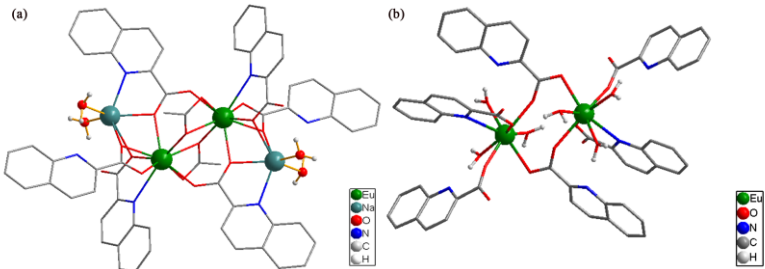


Fig. 2. Dinuclear “Eu-dimer” structure of compounds 1 (a) and 2 (b). Hydrogen atoms of organic ligand are omitted for clarity

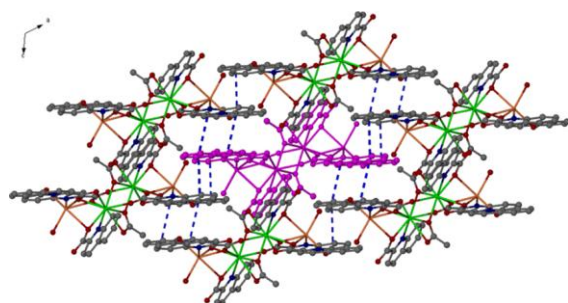


Fig. 3. Packing diagram of compound 1

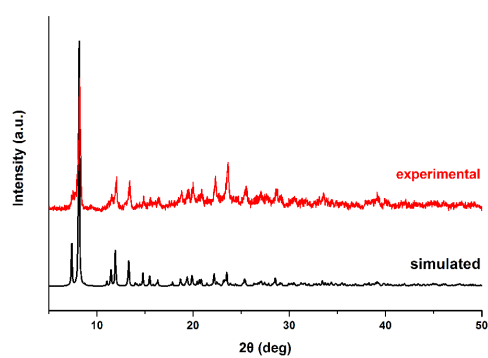


Fig. 4. Powder X-ray diffraction pattern for compound 1

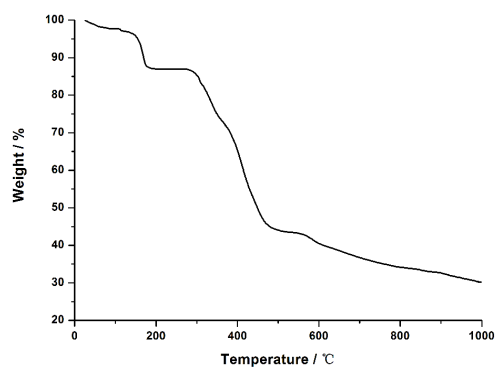


Fig. 5. TGA diagram for compound 1

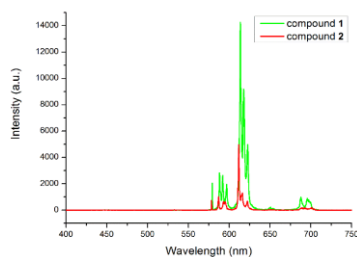
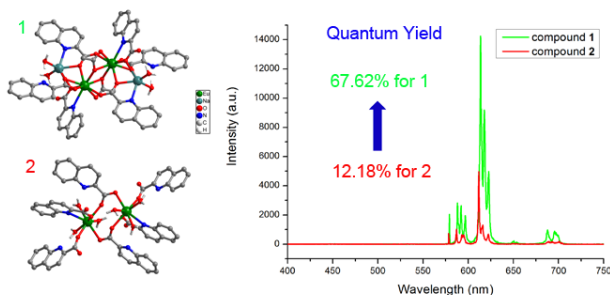


Fig. 6. Emission spectra of compounds **1** and **2** in the solid state excited at 350 nm

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Two Eu^{3+} compounds based on quinoline-2-carboxylic acid (Hqc), featuring in similar dinuclear structures with compositions of $[\text{Na}_2\text{Eu}_2(\text{qc})_6(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_4]\cdot 2\text{DMF}$ (**1**) and $[\text{Eu}_2(\text{qc})_6(\text{H}_2\text{O})_6]\cdot 3\text{H}_2\text{O}$ (**2**), have been successfully synthesized and optically studied. The quantum yield amounts to 67.62% within compound **1** that is 5.5 times as much as that of **2** (12.18%), since the Eu^{3+} ion in **1** is better protected by the coordinated acetic acid and sodium ion nearby to keep coordinated water molecules away from the coordinated sphere, through which it reduces the nonradiative deactivation process.